D8a

(19) Japanese Patent Office (JP)

(12) Laid-Open Patent Publication (A)

(11) Patent Application Publication No. Sho 63-100042

(43) Publication date: Showa 63 (1988) May 2

(51) Int.Cl⁴	Identification symbol	Internal Reference No.
C 03 C 17/23		8017-4G

Request for examination Not yet filed
Number of invention(s) 1 (Total 3 pages)

(54) Title of the invention Difficultly stainable glass product

(21) Patent Application Sho 61-243762
(22) Filing date Sho 61 (1986) October 14

(72) Inventor Shin Kume
c/o Nihon Itagarasu K.K., 8, Dosho-machi 4-chome, Higashi-ku, Osaka-shi, Osaka-fu

(72) Inventor Takashi Nozu
c/o Nihon Itagarasu K.K., 8, Dosho-machi 4-chome, Higashi-ku, Osaka-shi, Osaka-fu

(71) Applicant Nihon Itagarasu K.K., 8, Dosho-machi 4-chome, Higashi-ku, Osaka-shi, Osaka-fu

(74) Agent Seiichi Ohno, Patent Attorney

SPECIFICATION

1. Title of the invention

Difficultly stainable glass product

2. Scope of claim for patent

(1) A difficultly stainable glass product characterised in that a titanium dioxide thin film, to which a minute amount of Pt, Rh or Pd is added, have been formed on the surface thereof.

3. Detailed description of the invention

[Utilizable field in industry]

This invention relates to a glass product, particularly to a difficultly stainable glass product used for windows of a building or vehicles, and others.

[Prior art]

To the surface of a usual window glass exposed to air, oils such as an aliphatic acid, etc. or organic stains such as a tar component caused by an exhaust gas of automobiles are adhered, and thus, when water drops are attached to a window glass, the glass shows water repellency and transparency is inhibited. (Tsuchihashi, "Surface Chemistry of Glass" Nankodo, 1958; Ohba, "Glass Surface Planning", Kindai Henshusha, 1983, page 201)

Also, a glass surface to which organic stains are adhered becomes water repellency, and when water containing silicates is contacted with it due to rain, etc., drops are formed which are hardly drip so that after evaporation of water, insoluble silicate compounds are precipitated on the glass surface whereby firm stain is likely formed.

Further, such organic stains are likely adhered to the glass surface ununiformly, and thus, water component in air is likely condensed on the glass surface, which becomes a cause of forming the so-called discoloration. (Tsuchihashi, Surface Chemistry of Glass, page 50). Thus, it was required to conduct an operation to clean the glass by using a cleanser or an organic solvent frequently.

[Problems to be solved by the invention]

An object of the present invention is to provide a glass product having an ability of keeping the surface always clean by

rapidly and automatically decomposing and removing organic stains adhered to the glass surface as mentioned above.

[Means for solving the tasks]

In order to accomplish the above object, the present invention comprises forming a titanium dioxide thin film to which a minute amount of Pt, Rh or Pd is added on the surface of a glass product.

As the method for forming the above-mentioned thin film, it can be carried out by using known techniques such as the CVD method, the spray method, the sol-gel method, the dipping method, the vacuum deposition method or the sputtering method, etc.

Also, on the surface of a glass product on the surface of which is already formed a titanium dioxide thin film with a thickness of about 0.05 μm, for example, a heat rays-reflecting glass such as a trade name of "Reflight S" (available from Nihon Itagarasu K.K.), a minute amount of Pt, Rh, or Pd may be coated. As the coating method of this case, known techniques as mentioned above may be used, but it can be carried out by the light deposition method. This method itself is known. (see, for example, Applied Physics, vol. 53, pp. 916-933 (1984).)

[Action]

When a light having a wavelength of about 450 nm or less is irradiated to the glass product of the present invention, organic stains adhered to the glass surface are decomposed by oxidization due to the so-called light catalytic action of the titanium dioxide thin film. That is, due to light irradiation, electrons and positive pores occur inside the titanium dioxide thin film which is a semiconductor, they move to the surface of the thin film and react with organic substances and water adhered to the surface and the organic substances are oxidized to finally become CO_2. At this time, when superfine particles of Pt, Rh, or Pd are carried on the titanium dioxide thin film, efficiency of the above-mentioned light catalytic action is remarkably improved. This has already been reported about titanium dioxide fine particles, and the present inventors have

found similar effects in the case of the titanium dioxide thin film.

[Examples]

In Table 1, coating conditions by the spray method and the light deposition method are shown. Attached amount of Pt, Rh, or Pd is 2 to 40 mg/m^2. In Table 2, a composition of the coating solution is shown. And in Fig. 1, change in a contact angle with water was shown relative to light irradiation time by a 500 W high pressure mercury lamp to respective glass samples exposed to air. Measurement of the contact angle was carried out by an contact angle meter CA-D (produced by Kyowa Kaimen Kagaku). A distance from the lamp to the samples was made 20 cm.

Here, Comparative example 1 is a usual float plate glass, and Comparative example 2 is Reflight S (titanium dioxide coating glass plate).

In the glass sample prepared according to the present invention, it can be admitted that the contact angle is rapidly lowered as compared with the comparative examples. That is, the surface which was firstly water repellency became easily wet to water since stain due to organic substances are decomposed and removed by the light catalytic action.

As can be seen from the above, in the glass plate in accordance with the present invention, a contact angle with water is extremely small under the usual using conditions, i.e., easily wet, and thus, it is clear that it becomes extremely difficultly stainable.

Table 1

No.	Glass	Coating method	Coating solution
1	Float plate glass	.....	—
2	Reflight S	.....	—
3	Reflight S	Spray method	A
4	Reflight S	Light deposition method	B
5	Reflight S	Light deposition method	C

Table 1 (contd.)

No.	Glass	Coating method	Coating solution
6	Float plate glass	Spray method	D
7	Reflight S	Light deposition method	E

Table 2

A	N,N-dimethylformamide	100 parts
	Platinum chlorobenzonitrile	0.10 part
B	Water	80 parts
	Ethyl alcohol	20 parts
	Rhodium chloride	0.15 part
C	Water	80 parts
	Ethyl alcohol	20 parts
	Palladium chloride	0.20 part
D	N,N-dimethylformamide	100 parts
	Titanium acetylacetone	1.0 part
	Platinum chlorobenzonitrile	0.10 part
E	Water	80 parts
	Ethyl alcohol	20 parts
	Potassium chloroplatinate	0.05 part

[Effects of the invention]

As described in detail above, the glass of the present invention is coated by a titanium dioxide thin film to which a minute amount of platinum, rhodium or palladium is added so that organic stains attached to the glass surface are rapidly decomposed by the action of ultraviolet rays whereby it shows an extremely difficultly stainable property. Also, as the producing method, the CVD method, the sputtering method, the spray method, etc. can be utilized so that the above-mentioned

thin film can be coated on the large sized glass plate with a muss production system.

[Brief description of the drawings]

Fig. 1 is a graph showing change in a contact angle with water in relation to an irradiation time of a high pressure mercury lamp (400 W). No. 1: Comparative example (Float plate glass), No. 2: Comparative example (Reflight S), No. 3 to No. 7: Examples of the present invention.

Applicant for patent	Nihon Itagarasu K.K.
Agent	Seiichi Ohno, Patent Attorney (sealed)

Fig. 1

Contact angle

Irradiation time (hr)

JAPANESE PATENT KOKAI 63-100042

Japanese Patent Office (JP)
Patent Application Laid Open
JAPANESE PATENT KOKAI (A) 63-100042
Published 2nd May 1988

International Classification	Recognition Code	Office Handling Number
C 03 C 17/23		8017-4G

Request for Examination: Not yet requested
Number of Inventions: One
Number of Pages in the Japanese Text: Three

Title of the Invention: Glass products which are not liable to contamination

Application Number: 61-243762
Date of Application: 14th October 1986

Inventor: Makoto Kume
c/o Nippon Ita Garasu K.K., 8 Doshumachi-4-chome, Higashi-ku, Osaka-shi, Osaka-fu, Japan
Inventor: Takashi Nozu
c/o Nippon Ita Garasu K.K., 8 Doshumachi-4-chome, Higashi-ku, Osaka-shi, Osaka-fu, Japan
Applicant: Nippon Ita Garasu K.K.
8 Doshumachi-4-chome, Higashi-ku, Osaka-shi, Osaka-fu, Japan
Agent: Patent Attorney K. Ono

SPECIFICATION

1. Title of the Invention

Glass products which are not liable to contamination

2. Scope of the Patent Claims

1) Glass product which is not liable to contamination, characterized in that a thin film of titanium dioxide to which a trace amount of Pt, Rh and/or Pd has been added is formed on the surface.

3. Detailed Description of the Invention

Industrial Field of Application

The invention concerns glass products, and especially glass products which not liable to contamination, which can be used as windows in buildings and vehicles and in other applications.

Prior Art

Contamination with various organic materials including oily components such as fatty acids and the tar-like materials produced by automobile exhausts becomes attached to the surface of window glass which is generally exposed to the atmosphere and, as a result of this, visibility is reduced because of the strongly water repellant nature of the surface of the window glass and the formation of water droplet. (Tsuchibachi, "The Surface Chemistry of Glass" (Japanese), published by Nankodo, 1958; Oba, "Glass Surface Design" (Japanese), published by the Kindai Henshu Co., 1983, page 201)

Furthermore, a glass surface to which organic material contamination has become attached is water repellant and so water droplets are formed when water which contains silicates due to rain etc. makes contact and these can run down only with difficulty and the insoluble silicate compounds etc. are likely to be precipitated out on the glass after the water has evaporated with the formation of solid contamination.

Moreover, such organic contamination is likely to be deposited heterogeneously on the glass surface and so

there is a problem in that the moisture in the atmosphere is liable to condense on the glass surface and so-called misting is liable to occur (Tsuchihachi, "The Surface Chemistry of Glass" (Japanese), published by Nankodo, 1958, page 50). Consequently the glass must be cleaned regularly using a detergent or an organic solvent.

Problems to be Resolved by the Invention

The invention is intended to provide glass products with which the organic contamination which becomes attached to the glass surface in the way described above is quickly and automatically broken down and eliminated, and which have the capacity generally for the surface to remain clean.

Means of Resolving These Problems

In order to achieve the aforementioned objective, the present invention is characterized in that a thin film of titanium dioxide to which Pt, Rh and/or Pd has been added in a trace amount is formed on the surface of the glass product.

Any of the known methods, such as the CVD method, the spray method, the sol-gel method, the immersion method, the vacuum vapour deposition method or the sputtering method for example, can be used to form the abovementioned thin film.

Furthermore, trace amounts of Pt, Rh or Pd may be coated on the surface of a glass product on the surface of which a thin film of titanium dioxide of thickness about 0.05 μm has been formed beforehand, for example on the surface of infrared reflecting glass such as "Refuraito S" (trade name, Nippon Ita Garasu CO.). The known coating techniques indicated above can be used for coating in this case, but coating can also be achieved using the photodeposition method. The method itself is known (for example, see Oyo Butsuri, Vol.53, pages 916 to 933 (1984))

Action

If light of wavelength below about 450 nm is

directed onto a glass product of this invention then the organic material contamination which is attached to the glass surface is oxidatively degraded by the so-called photocatalytic action of the thin film of titanium dioxide. That is to say, electrons and positive holes are generated within the thin layer of titanium dioxide, which is a semiconductor, as a result of irradiation with light and these migrate to the surface of the thin film and react with the organic material and moisture which is attached to the surface, and the organic material is oxidized and ultimately becomes CO_2. If ultra-fine grains of Pt, Rh or Pd are loaded onto the thin titanium dioxide film at this time then the efficiency of the above-mentioned photocatalytic action is markedly improved. This fact has been reported before in connection with fine particles of titanium dioxide, and the inventors have discovered the same effect can also be realized with a thin film of titanium dioxide.

Illustrative Examples

The coating conditions, with the spray method or the photodeposition method, are shown in Table 1. The amount of Pt, Rh and/or Pd attached was from 2 to 40 mg/m^2. The compositions of the coating liquids are shown in Table 2. The change in the angle of contact with water with respect to the duration of irradiation with light from a 500 W high pressure mercury lamp of each glass sample which had been exposed to the atmosphere is shown in Figure 1. Measurement of the angle of contact was carried out using a contact angle meter CA-D (manufactured by Kyowa Kaimen Kagaku). The lamp - sample distance was set at 20 cm.

Comparative Example 1 was normal front windshield glass and Comparative Example 2 was Refuraito S (titanium dioxide coated glass).

With the glass samples which had been made in accordance with the invention the angle of contact was seen to fall rapidly when compared with the comparative

examples. That is to say, the surface which was initially water repellant became easily wet with water because the organic material contamination was degraded and eliminated by the photocatalytic action.

As seen above, with glass sheets which conformed with the invention the contact angle with water under normal use conditions was very low, which is to say that the glass is easily wetted, and so it is clear that it is very difficult for the glass to become contaminated.

Table 1

No.	Glass	Coating Method	Coating Liquid
1	Front Glass	-	-
2	Refuraito S	-	-
3	Refuraito S	Spray method	A
4	Refuraito S	Photodeposition	B
5	Refuraito S	Photodeposition	C
6	Front Glass	Spray method	D
7	Refuraito S	Photodeposition	E

Table 2

A:	N,N-Dimethylformamide	100 parts
	Chlorobenzonitrile platinum	0.10 part
B:	Water	80 parts
	Ethyl alcohol	20 parts
	Rhodium chloride	0.15 part
C:	Water	80 parts
	Ethyl alcohol	20 parts
	Palladium chloride	0.20 part
D:	N,N-Dimethylformamide	100 parts
	Titanium acetylacetone	1.0 part
	Chlorobenzonitrile platinum	0.10 part
E:	Water	80 parts
	Ethyl Alcohol	20 parts
	Potassium chloroplatinate	0.05 part

Effect of the Invention

As described above, glass of this invention has a nature such that it very unlikely to become contaminated since, as a result of being coated with a thin film of titanium dioxide to which a trace amount of platinum, rhodium and/or palladium has been added, any organic

material attached to the glass surface is rapidly degraded by the action or ultraviolet radiation. Furthermore, the abovementioned thin films can be coated on a large surface area of glass sheet with a mass production system using a CVD method, a sputtering method or a spray method, for example, as the method of manufacture.

Brief Explanation of the Drawing

Figure 1 is a graph which shows the change in the angle of contact with water with respect to the period of irradiation with a high pressure mercury lamp (400 W). No.1: Comparative example (front windshield glass), No.2: Comparative example (Refuraito S), Nos.3 to 7: Illustrative examples of the invention.

Applicant: Nippon Ita Garasu K.K.

Agent: Patent Attorney K. Ono

Figure 1